comparison with cetyl pyridinium chloride (CPC) is of interest. *N*-Methyl-pyrrolidinium tetraphenylboron, our most biologically-active amide derivative, compares favorably with CPC in activity against gram-positive bacteria and fungi (Active at 1–10 μg./ml.).

EXPERIMENTAL

Preparation of derivatives. Approximately 250-mg. samples of each compound were dissolved or suspended in 20 ml. of water that was then adjusted to *p*H 2.0 with dilute hydrochloric acid. Several drops of 0.1% aluminum chloride solution were added to aid in the final precipitation. To the solutions heated at 60° in a water bath, an excess of 0.6% sodium tetraphenylboron solution was added. The precipitate was allowed to settle at room temperature; was filtered and washed with water, and dried at 60° *in vacuo,* and the melting point of the derivative was determined.

Melting points were determined on a Kofler micro hot stage with a calibrated thermometer. Dumas nitrogen determinations were made on all derivatives.

Starting materials. 5-Methyl-2-pyrrolidone was kindly supplied by the Quaker Oats Company; *N*-vinylpyrrolidone, polyvinylpyrrolidone (mol. wt. 50,000), and *N*-methylpyrrolidone-2 were supplied by the General Aniline and Film Corporation. Acrylamide was furnished by the American Cyanamid Company. *N*-Allyl-γ-hydroxybutyramide and *N*-allyl-pyrrolidone-2 were synthesized from butyrolactone and allylamine according to the method of Spath and Lintner.[7] The other amides were purchased from commercial sources.

Acknowledgment. The authors wish to thank Earl Huber for technical assistance and Alfred Foulds for the microanalysis.

RESEARCH LABORATORIES
J. T. BAKER CHEMICAL COMPANY
PHILLIPSBURG, N. J.

---

[7] E. Spath and J. Lintner, *Ber.*, 69, 2730 (1936).

An Attempt to Form a Grignard Reagent in Phenyl Ether

GEORGE S. HANDLER[1]

Received January 20, 1959

During the course of some studies of the Grignard reagent, an attempt was made to prepare the reagent in phenyl ether by the usual methods. The attempt failed in a rather interesting fashion. A reaction took place, but it was not a Grignard reaction.

EXPERIMENTAL

Twelve and two-tenths grams of "Grignard-grade" magnesium (0.5 mole) was placed in a two-necked flask containing 348 g. of phenyl ether (2 moles). An addition funnel containing 75.0 g. of *n*-amyl bromide (0.5 mole) was placed on one neck and a Dry Ice–acetone trap on the other. Stirring was provided by a magnetic stirring apparatus and a Teflon covered stirring bar. A small amount of amyl bromide was added to the flask, which was then warmed. No reaction was observed. The flask was warmed further, more amyl bromide being added, until all the amyl bromide had been added and a temperature of about 65° was reached. Heating was continued until a reaction started at about 110–115°, as evidenced by the appearance of a white precipitate, and foaming. Since the possibility of Grignard formation was still being considered at that time, the reaction vessel was quickly cooled with an ice water bath kept handy for the purpose. The reaction stopped, and would continue only at elevated temperatures. The temperature was held at about 110–120° for 24 hr., until no amyl bromide could be refluxed. It was observed that only about half of the magnesium, originally present in stoichiometric amount based on the Grignard, had reacted.

The solution was centrifuged, the supernatant decanted, and the precipitate was washed three times with portions of dry benzene and dried. The precipitate was then treated with sufficient dilute HCl to react with all the magnesium, the reaction flask being separated from the atmosphere at all times by a cold water condenser topped by a Dry Ice–acetone trap. Only a trace of pentane could be collected. Attention was then turned to the supernatant fluid.

The next most likely possibility seemed to be that a Wurtz-type reaction had taken place, forming *n*-decane. (B.P. 174°) The fluid was heated past 174°. No decane distilled off.

Since all possibilities except direct addition to the ether seemed to have been eliminated, the fluid was vacuum-distilled at 13 mm. About three fourths of the fluid distilled over at 124°, after which the temperature rose to about 155°, remaining there for the remainder of the distillation. Infrared analysis of this latter cut showed a strong C—H peak. Several peaks in the 800–900 cm.$^{-1}$ region indicated the possibility of para substitution. Analysis by means of hyperfine proton magnetic resonance techniques indicated the presence of a sec-amyl group, again suggesting para substitution. Elemental analysis of the product gave C, 84.6%, and H, 8.7%. Theoretical analysis for an amylated phenyl ether is C, 84.6%, H, 8.8%. Yield was about 60%. The density was 1.073 gm./cm.^{3}; the index of refraction was 1.5771. An examination of recent literature failed to reveal data on this compound.

Later runs involving smaller quantities resulted in the evolution of about the correct amount of H_2 according to the overall reaction

$$2(C_6H_5)_2O + 2AmBr + Mg \longrightarrow 2\ C_6H_5O{-}C_6H_4Am + MgBr_2 + H_2$$

Recovery of excess magnesium was also made here. Magnesium was used according to the above reaction.

It seems clear that what actually happened was not a Grignard reaction, but a Friedel-Crafts alkylation of the ether. The Lewis acid here was $MgBr_2$, initially formed in trace quantities by some side reaction. The reaction itself produced more catalyst, so that once initiated, it proceeded smoothly.

The implications of this and certain other experiments with Grignard systems will be discussed in a forthcoming publication.

Acknowledgment. I wish to acknowledge several helpful discussions with Dr. R. E. Dessy, of the Department of Chemistry of the University of

---

[1] Present address: Dept. of Chemistry, Tufts University, Medford, Mass.

Cincinnati. Mr. J. H. Lady, of this laboratory, performed the infrared analysis; Dr. D. O'Reilly, of Gulf Research Laboratories, performed the NMR analysis; Mr. E. Pantier, of this laboratory, performed some of the runs and distillations.

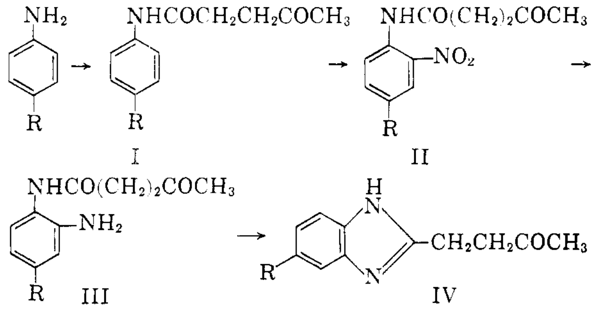
WESTINGHOUSE RESEARCH LABORATORIES
PITTSBURGH, PA.

Preparation of 5-Chloro- and 5-Bromo-2-(2-acetylethyl)benzimidazoles

TETSUO SUAMI[1] AND ALLAN R. DAY

Received February 6, 1959

In connection with other work on benzimidazoles, 2-acetylethylbenzimidazoles appeared to be of interest as potential antimetabolites and as starting materials for the preparation of other benzimidazole derivatives. The present paper describes the syntheses of two 2-acetylethylbenzimidazoles by the following route:



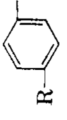
Six 4-substituted levulinanilides (I) were prepared by the acylation of 4-substituted anilines with γ-acetyoxy-γ-valerolactone (Table I). Lukes and Prelog[2] prepared levulinanilide and 4-methyllevulinanilide by this method.

The oximes of the levulinanilide derivatives (Table II) were prepared by the usual method using hydroxylamine hydrochloride and 2*N* sodium hydroxide solution.

The levulinanilide derivatives, reported in Table I, were nitrated with a sulfuric acid–nitric acid mixture, at −10 to −20° (Table III). The oximes of the nitro compounds were prepared also (Table IV).

For the determination of the position of the nitro group, the nitrolevulinanilide derivatives were hydrolyzed with dilute hydrochloric acid to the corresponding nitroaniline derivatives. 4-Nitro-

TABLE I



NHCOCH₂CH₂COCH₃

R	M.P., °C.	Yield, %	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Chlorine Calcd.	Chlorine Found	Bromine Calcd.	Bromine Found
Cl	149–151[a]	58.7	$C_{11}H_{12}NClO_2$	58.54	58.58	5.36	5.36	6.21	6.22	15.71	15.56		
Br	157–158[b]	57.6	$C_{11}H_{12}NBrO_2$	48.91	48.99	4.48	4.63	5.19	5.22			29.58	29.40
COOH	214–216[c] (dec.)	48.5	$C_{12}H_{13}NO_4$	61.27	61.29	5.57	5.40	5.96	5.98				
$COOC_2H_5$	108–109[d]	28.8	$C_{14}H_{17}NO_4$	63.85	63.72	6.51	6.59	5.32	5.28				
$NHCOCH_3$	201–202[e] (dec.)	49.5	$C_{13}H_{16}N_2O_3$	62.89	62.75	6.50	6.65	11.29	11.23				
$NHCO(CH_2)_2COCH_3$	217–218[c]	37.8	$C_{16}H_{20}N_2O_4$	63.16	63.05	6.63	6.57	9.21	9.14				

[a] Recrystallized from 95% ethanol. [b] Recrystallized from methanol. [c] Recrystallized from water. [d] Recrystallized from ethyl acetate-ether. [e] Recrystallized from 1-butyl alcohol.

---

[1] Assistant Professor of Keio University (Tokyo, Japan). Postdoctoral Research Associate in the Department of Chemistry, University of Pennsylvania (1957–58).

[2] R. Lukes and V. Prelog, *Collection Czechoslov. Chem. Communs.*, 1, 282 (1929).